



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US95/14429 <b>(22) International Filing Date:</b> 8 November 1995 (08.11.95)  <b>(30) Priority Data:</b> PM 9304 9 November 1994 (09.11.94) AU  <b>(71) Applicants (for all designated States except US):</b> E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANIZATION [AU/AU]; 407 Royal Parade, Parkville, VIC 3052 (AU).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> MOAD, Graeme [AU/AU]; 137 Monbulk Road, Kallista, VIC 3791 (AU). MOAD, Catherine, Louise [US/AU]; 137 Monbulk Road, Kallista, VIC 3791 (AU). KRSTINA, Julia [AU/AU]; 16B Elsie Grove, Chelsea, VIC 3196 (AU). RIZZARDO, Ezio [AU/AU]; 26 Alex Avenue, Wheelers Hill, VIC 3150 (AU). THANG, San, Hoa [AU/AU]; 180 Clarinda Road, Clayton South, VIC 3169 (AU). FRYD, Michael [US/US]; 50 East Maple Avenue, Moorestown, NJ 08057-1910 (US).		<b>(74) Agents:</b> COSTELLO, James, A. et al.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).  <b>(81) Designated States:</b> AL, AM, AU, BB, BG, BR, BY, CA, CN, CZ, EE, FI, GE, HU, IS, JP, KG, KP, KR, KZ, LK, LR, LT, LV, MD, MG, MK, MN, MX, NO, NZ, PL, RO, RU, SG, SI, SK, TJ, TM, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, LS, MW, SD, SZ, UG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> POLYMERIZATION IN AQUEOUS MEDIA  <b>(57) Abstract</b>  A method for the solution or emulsion polymerization of ethylenically unsaturated monomers, styrene, and other free radical polymerizable monomers in aqueous media in which a cobalt chain transfer agent is used which has both hydrolytic stability and solubility in water and in the organic phase with preferential solubility in the organic phase.		

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## POLYMERIZATION IN AQUEOUS MEDIA

5        This invention relates to free-radical polymerization in emulsion or in aqueous solution to produce polymers with defined molecular weight and end group structures and to certain cobalt complexes employed in the polymerization process.

US 5 324 879 discloses the use of cobalt(III) complexes to control molecular weights in free radical polymerization. US 4 694 054 discloses the use of certain Co(II) complexes in emulsion polymerization.

This invention concerns a method for the solution or emulsion polymerization in aqueous media of at least one monomer selected from the group

- 20
- a) 1,1-disubstituted ethylenically unsaturated monomer;
  - b) styrene;
  - c) a mixture of a and b; and
  - d) a mixture of at least one of a and b with one or more other free radical polymerizable monomers;

said monomer or monomer mixture comprising at least 50 percent by weight of monomer selected from at least one of a and b;

25 comprising contacting the following materials:

- i) water or a single phase water-organic solvent mixture,
- ii) at least one monomer selected from a to d,
- iii) a cobalt chelate chain transfer agent,
- iv) an optional surfactant for emulsion polymerization,
- v) an optional free radical initiator soluble in the media;

wherein the cobalt chelate chain transfer agent has the following properties:

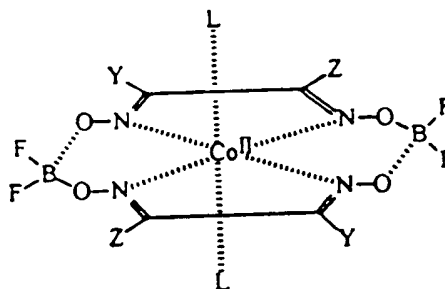
- vi) hydrolytic stability, and
- vii) solubility in water and in the organic phase, with preferential solubility in the organic phase.

We have discovered that certain types of cobalt complexes are most effective in controlling the molecular weights in emulsion polymerization or in aqueous solution. These complexes act as efficient catalytic chain transfer agents

and produce polymers with unsaturated chain ends. Either cobalt (II) complexes or cobalt (III) complexes can be utilized in the present invention. The reaction conditions are extremely important in determining the success of the experiment and must be chosen with regard to the complex used.

- 5 This invention provides a process whereby free radical polymerization can be readily carried out in aqueous or part aqueous media to produce macromonomers. Such macromonomers are oligomeric or homo- or copolymers containing unsaturation at a terminus. The macromonomers are of low color and have a high degree of terminal unsaturation. The process of the invention utilizes  
 10 free radical polymerization in the presence of a metal complex which gives catalytic chain transfer and which in addition has ligands necessary to convey the necessary hydrolytic stability and solubility parameters. Complexes suitable for emulsion polymerization have solubility in both the organic and aqueous phases and partition in favor of the organic phase. Complexes suitable for aqueous solution  
 15 polymerisation are soluble in water-monomer or water-monomer-cosolvent mixtures.

- A list of preferred complexes is shown below. It will be obvious to those skilled in the art that any metal complex which gives catalytic chain transfer and which in addition has ligands necessary to convey the necessary hydrolytic stability  
 20 and solubility parameters may be used in the present invention. Preferred complexes are those selected from square planar cobalt(II) and cobalt(III) chelates.



25

Co(II)(DPG-BF<sub>2</sub>)<sub>2</sub>

Y=Z=Ph, L=ligand

Co(II)(DMG-BF<sub>2</sub>)<sub>2</sub>

Y=Z=Me, L=ligand

Co(II)(EMG-BF<sub>2</sub>)<sub>2</sub>

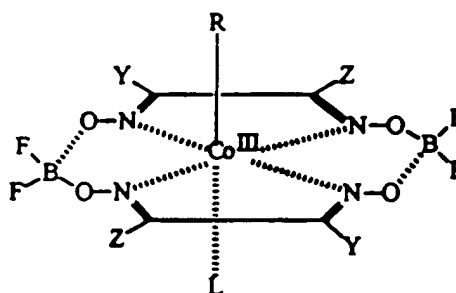
Y=Me, Z=Et, L=ligand

Co(II)(DEG-BF<sub>2</sub>)<sub>2</sub>

Y=Z=Et, L=ligand

30

Co(II)(CHG-BF<sub>2</sub>)<sub>2</sub>Y+Z=-(CH<sub>2</sub>)<sub>4</sub>- (cyclohexyl), L=ligand.



	$\text{RCo(III)(DPG-BF}_2)_2$	$\text{Y=Z=Ph, R= alkyl, L=ligand}$
5	$\text{RCo(III)(DMG-BF}_2)_2$	$\text{Y=Z=Me, R= alkyl, L=ligand}$
	$\text{RCo(III)(EMG-BF}_2)_2$	$\text{Y=Me, Z=Et, R= alkyl, L=ligand}$
	$\text{RCo(III)(DEG-BF}_2)_2$	$\text{Y=Z=Et, R= alkyl, L=ligand}$
	$\text{RCo(III)(CHG-BF}_2)_2$	$\text{Y+Z=-(CH}_2)_4\text{- (cyclohexyl), R= alkyl, L=ligand}$
	$\text{RCo(III)(DMG-BF}_2)_2$	$\text{Y=Z=Me, R= halogen, L=ligand.}$

10

The cobalt (III) complexes based on  $\text{BF}_2$ -bridged 3,4-hexandione dioxime, 2,3-pentandione dioxime and 1,2-cyclohexanedione dioxime ligands are designed to give improved stability and/or solubility parameters.

15 Cobalt(II) complexes [for example,  $\text{Co(II)(DMG-BF}_2)_2$ ], although effective in emulsion polymerization, have disadvantages when used directly because of their extreme sensitivity to air. It is, therefore, preferable to use cobalt(III) complexes [for example,  $\text{iPrCo(III)(DMG-BF}_2)_2$ ] which generate the active cobalt(II) species *in situ* under the reaction conditions. In the case of most  
20 alkyl cobalt (III) complexes this involves homolytic scission of the cobalt-R bond.

Other complexes that can be used include cobalt(III) complexes which are reduced to cobalt (II) complexes in a bimolecular process involving reaction with other species in the reaction medium [for example,  $\text{ClCo(III)(DMG-BF}_2)_2$  or  $\text{MeCo(III)(DEG-BF}_2)_2$ ]. Cobalt(III) complexes which are not as readily  
25 converted to cobalt (II) complexes [for example  $\text{MeCo(III)(DMG-BF}_2)_2$ ] are less effective in controlling molecular weight.

### DETAILS OF THE INVENTION

To achieve best control over molecular weight, the ligands (L) are selected  
30 to suit the reaction conditions (monomers, cosolvents, surfactant, reaction temperature, etc.). L is selected from Lewis bases including tertiary amines (such as pyridine), water, ether, phosphines, and the like, as will be obvious to one

skilled in the art. The use of the cobalt (II) complexes [for example  $\text{Co(II)(DMG-BF}_2)_2$ ] gives poor results with hydroxy and acid monomers [for example HEMA or MAA]. The use of the corresponding cobalt(III) complexes,  $\text{iPrCo(III)(DMG-BF}_2)_2$  or  $\text{MeCo(III)(DEG-BF}_2)_2$ , which are compatible with hydroxy and acid monomers, gives good results.

The activity of the cobalt(III) complexes shows less dependence on surfactant type than is seen with cobalt(II) complexes. Depending on the reaction conditions cobalt(III) complexes are up to 3-20 fold more active than the corresponding cobalt(II) complexes in reducing molecular weight in emulsion polymerization. Although use of a surfactant (iv) may be desirable, such use is not necessary for self-stabilizing systems or systems otherwise stable such as by employment of block or graft copolymer stabilizers.

An important factor in controlling activity in emulsion polymerization is the solubility of the complex in aqueous and organic media. The complex should be soluble in both the organic and aqueous phases and the partition coefficient between the aqueous and organic phases should be in favor of the organic phase. Complexes based on diethyl glyoxime [for example,  $\text{iPrCo(III)(DEG-BF}_2)_2$ ] are more active than those based on dimethyl glyoxime [for example,  $\text{iPrCo(III)(DMG-BF}_2)_2$ ].

However, some water solubility is required for the complex to distribute through the reaction mixture. The diphenyl glyoxime complexes [for example,  $\text{Co(II)(DPG-BF}_2)_2$  and  $\text{MeCo(III)(DPG-BF}_2)_2$ ] show much reduced activity with respect to corresponding dimethyl glyoxime complexes [for example  $\text{Co(II)(DMG-BF}_2)_2$  and  $\text{iPrCo(III)(DMG-BF}_2)_2$ ].

Higher complex concentrations are required for molecular weight control with very hydrophobic monomers, for example BMA or styrene. This result is most likely due to the lower solubility of the complex in the organic phase. Use of the term "styrene" herein is intended to include substituted styrenes as well.

Another important factor is the stability of the complex to hydrolysis. Incremental addition of the complex during the reaction improves molecular weight control especially in polymerizations of acid monomers (e.g. MAA) or with acidic reaction conditions. For both cobalt(II) and cobalt(III) glyoxime complexes,  $\text{BF}_2$ -bridging improves the hydrolytic stability of the complexes. The use of lower reaction temperatures is also advantageous.

Water soluble azo-compounds, for example 4,4'-azobis(cyanovaleric acid), are the preferred initiators for emulsion polymerization and for aqueous solution polymerization. Faster decomposing azo compounds, for example, WAKO V-44 [2,2'-azobis(N,N'-dimethyleisobutyramidine) dihydrochloride], allow use of

lower reaction temperatures (50–60°C) and are preferred for polymerizations involving methacrylic acid. Organic soluble azo-compounds can also be used for emulsion polymerization in some cases.

5 The preferred monomers for use with this invention are  $\alpha$ -methylvinyl and styrenic monomers, mixtures of these monomers and mixtures of these monomers with other unsaturated monomers including acrylic monomers. The preferred  $\alpha$ -methylvinyl monomers include: alkyl methacrylates (*e.g.* MMA, EMA, *n*-BMA, *i*-BMA, 2-EHMA, PhMA, *etc.*) substituted alkyl methacrylates (*e.g.* HEMA, GMA, *etc.*), methacrylic acid (*e.g.* MAA), *etc.*

10 In emulsion polymerization, a wide range of surfactants and surfactant concentrations have been used in conjunction with cobalt(III) complexes. Both ionic and non-ionic surfactants may be employed. These surfactants include SDS, ADS, AerosolMA, Teric N40, Teric NX40L, alkanate, AerosolOT/Teric N40 and similar surfactants. These surfactants may be used alone or in combination.

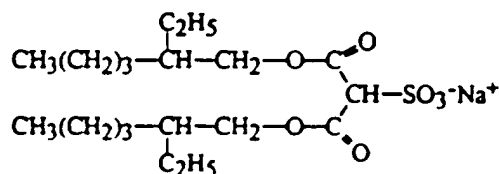
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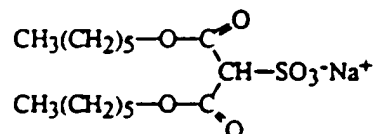
SDS



ADS

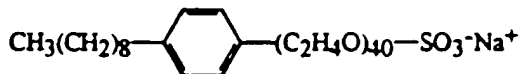


Aerosol OT



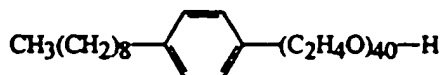
Aerosol MA80

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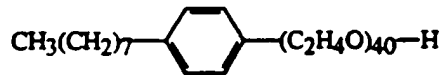


Teric 35N5 (Alkanate)

25



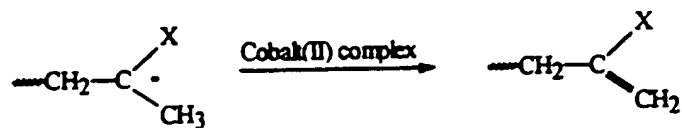
Teric N40



Teric NX40L

This invention will lead to polymers with a high degree of terminal unsaturation (typically in excess of 90%). Polymers formed with  $\alpha$ -methyl vinyl monomers ( $\text{CH}_2=\text{C}(\text{CH}_3)\text{X}$ ) will have the following end-group structure.

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The products can thus be used as macromonomers in a wide variety of applications. The end group functionality of the low molecular weight methacrylate ester polymers formed by the processes described can be established quantitatively by NMR spectroscopy or by thermogravimetric analysis. Some typical results are as follows. Within experimental error, there is one unsaturated end group per molecule.

15

**Table 1. End Group Functionality in Macromonomers**

Macromonomer	complex <sup>a</sup>	$\bar{M}_n^b$	end groups/molecule <sup>c</sup>
MMA	iPrCo(III)(DMG-BF <sub>2</sub> ) <sub>2</sub>	1400	1.04
MMA	MeCo(III)(EMG-BF <sub>2</sub> ) <sub>2</sub>	2100	0.98
MMA	MeCo(III)(DEG-BF <sub>2</sub> ) <sub>2</sub>	2400	0.98
HEMA	iPrCo(III)(DMG-BF <sub>2</sub> ) <sub>2</sub>	810	0.97

20

<sup>a</sup> cobalt complex used in macromonomer synthesis.

<sup>b</sup> GPC number average molecular weight.

<sup>c</sup> unsaturated chain end as estimated by NMR.

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Some of general advantages of polymerisation in emulsion and aqueous solution polymerisation is organic solutions have been delineated above. A further unexpected and important advantage of forming macromonomers in aqueous or part-aqueous media is that the products have substantially less color than those formed in organic media. Color is extremely important in many applications, for example, clear and light colored coatings and other materials.

30

Illustrative of the invention are the following examples showing the dependence of molecular weight on the type of complex, surfactant and comonomers employed; application to copolymer synthesis; and aqueous solution polymerisation of methacrylic acid and 2-hydroxyethyl methacrylate.

35



Key	
MMA	methyl methacrylate
HEMA	hydroxyethyl methacrylate
nBMA	n-butyl methacrylate
tBMA	t-butyl methacrylate
PhMA	phenyl methacrylate
2-EHMA	2-ethylhexyl methacrylate
MAA	methacrylic acid
MAM	methacrylamide
GMA	glycidyl methacrylate

**EXAMPLES 1-10****Emulsion polymerization with cobalt (II) complexes****5 Initial Charge:**

Solution 1:	Water	733 g
	Surfactant solution (30% w/v)	10.14 g
	4,4'-azobis(cyanovaleric acid)	1.32 g

10 Solution 2:	iPrCo(III)(DMG-BF <sub>2</sub> ) <sub>2</sub>	0.0176 g
	MMA	35.2 g

Solution 3:	MMA	317 g
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15 Solution 4:	Water	90 g
	Surfactant solution (30% w/v)	10.98 g

20 Solution 1 was degassed over 30 minutes and heated to 80°C when solution 2 and 10% of solution 4 was added in one shot. Solution 3 and the remaining solution 4 were then added over 90 min. The reaction temperature was then held for a further 90 min. The results of this and similar experiments are summarized in Table 2.

**Table 2. Effect of Complex, Surfactant and Initiator, Cobalt (II) Complexes**

Example	Complex	Conc (ppm)	Initiator	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	Surfactant	Particle size
5	none	0	0.27% V5010	177100	2.1	1.4% ADS	99
	1 Co(II)DPG	50	0.27% V5010	151000	2.2	1.4% ADS	87
	2 Co(II)DMG	5	0.27% V5010	192600	2.1	1.4% ADS	93
	3	50	0.27% V5010	171400	1.8	1.4% ADS	95
10	4 Co(II)DPG	50	0.27% V5010	179000	2.3	1.4% SDS	80
	5 Co(II)DMG	50	0.27% V5010	20000	1.8	1.4% SDS	281
	6	100	0.27% V5010	16100	2.5	1.4% SDS	407
15	none	0	0.1% V5010	585600	2.3	1.4% SDS	115
	7 Co(II)DMG	50	0.1% V5010	70600	2.4	1.4% SDS	322
	8	0	0.1% V5010	452500	2.1	6% SDS	68
	9 Co(II)DMG	50	0.1% V5010	48200	2.1	6% SDS	206
20	10	100	0.1% V5010	38400	2.6	6% SDS	276
	none	0	0.1% APS	132152	3.3	1.4% SDS	148
	10 Co(II)DMG	50	0.1% APS	64768	1.7	1.4% SDS	118

<sup>a</sup> initiators: APS ammonium persulphate; V5010 4,4'-azobis(cyanovaleric acid)

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**EXAMPLES 11-33**

Emulsion polymerization with cobalt (III) complexes (with surfactant feed)

30	Solution 1:	Water	75 g
		Surfactant solution (10% w/v)	3 g
		4,4'-azobis(cyanovaleric acid)	140 mg
35	Solution 2:	Surfactant solution (10% w/v)	1 g
		iPrCo(III)(DMG-BF <sub>2</sub> ) <sub>2</sub>	1.96 mg
		MMA	3.5 g
	Solution 3:	MMA	31.2 g
	Solution 4:	Surfactant solution (10% w/v)	8 g

Solution 1 was degassed over 20 minutes and heated to 80°C when solution 2 was added in one shot. The feeds (solution 3 and 4) were commenced and added over 90 min. The reaction temperature was then increased to 85°C and heating and stirring continued for a further 90 min. Results of this and similar experiments are summarized in Tables 3-5.

**Table 3. Effect of Complex on Emulsion Polymerisation of MMA<sup>a</sup>**

Example	Complex	conc ppm	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	% Conv	% coagulum
10	none	0	181000	2.5	100	-
11	Co(II)(DMG-BF <sub>2</sub> ) <sub>2</sub>	14	29900	2.4	95	5
12	iPrCo(III)(DMG-BF <sub>2</sub> ) <sub>2</sub>	17	10000	2.2	100	4
15	2-octyl Co(III)(DMG-BF <sub>2</sub> ) <sub>2</sub>	18	6200	1.7	34	4
14	iPrCo(III)(CHG-BF <sub>2</sub> ) <sub>2</sub>	16	18600	2.1	100	3
15	MeCo(III)(EMG-BF <sub>2</sub> ) <sub>2</sub>	16	6200	1.9	91	4
16	MeCo(III)(DEG-BF <sub>2</sub> ) <sub>2</sub>	16	3200	1.6	93	6
20	Co(II)(DPG-BF <sub>2</sub> ) <sub>2</sub>	22	119200	2.5	72	1
18	EtCo(III)(DPG-BF <sub>2</sub> ) <sub>2</sub>	24	30600	1.9	92	5

<sup>a</sup> 1% (w/v) SDS surfactant

Table 4. Effect of Surfactant on Emulsion Polymerization of MMA<sup>a</sup>

Table 4. Effect of Surfactant							
Example	Surfactant	wt% <sup>b</sup>	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	% Conv. <sup>d</sup>	% coagulum	
5	19	SDS	0.1	14200	2.5	100	11
	20	SDS	0.5	10600	3.2	92	4.
	21	SDS	1.0	10000	2.1	100	4
	22	SDS	3.0	8100	1.9	100	14
	23	ADS	1.0	16000	2.2	62	2
10	24	Aerosol MA80	1.0	13100	2.0	80	13
	25	SDS/Teric N40	0.1	11200	2.9	100	6
	26	SDS/Teric NX40L	0.1	12300	2.5	100	17
	27	alkanate	0.1	21000	2.0	88	13
	28	AerosolOT/Teric N40	0.1	12700	2.0	92	16
	29	AerosolOT/Teric NX40L	0.1	29800	2.2	91	12

15 a iPrCo(III)(DMG-BF<sub>2</sub>)<sub>2</sub> concentration 19 ppm.

b Surfactant level

Table 5. Effect of Comonomers on Emulsion Polymerization of MMA

Example	Comonomers	ratio	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	% Conv
20	none <sup>a</sup>	-	10000	-	100
	30 HEMA <sup>a,c</sup>	8:1	10600	2.0	75
	31 HEMA <sup>b,c</sup>	8:1	19000	3.0	
	32 MAA <sup>b</sup>	8:1	17600	2.6	90
	33 <i>n</i> -BMA:2-EHMA:MAA:HEMA:MAM <sup>a</sup>	d	8500	2.2	90

25 a 1% (w/v) SDS surfactant, iPrCo(III)(DMG-BF<sub>2</sub>)<sub>2</sub> concentration 17 ppm

b 1% (w/v) SDS surfactant, iPrCo(III)(CHG-BF<sub>2</sub>)<sub>2</sub> concentration 17 ppm

c control (no complex) gave  $\bar{M}_n$  119500,  $\bar{M}_w/\bar{M}_n$  6.9.

d ratio of monomers was 10:1:1:20:1

30

**EXAMPLES 34-49**

Emulsion polymerisation recipe (no surfactant feed)

Initial Charge:

35	Solution 1:	Water	75 g
		SDS solution (10% w/v)	3 g
		4,4'-azobis(cyanovaleric acid)	140 mg

<b>Solution 2:</b>	<b>iPrCo(III)(DMG-BF<sub>2</sub>)<sub>2</sub></b>	<b>2 mg</b>
	<b>MMA</b>	<b>3.5 g</b>

**Feed:** MMA 31.7 g

5

Water was degassed over 20 minutes and heated to 80°C when solution 2 was added in one shot. The MMA feed was then added over 90 min. The reaction temperature was then increased to 85°C and heating and stirring continued for a further 90 min. Results are summarized in Tables 6 and 7.

10

**Table 6. Emulsion Polymerisations of MMA - dialkylglyoxime based complexes<sup>a</sup>**

Example	Complex	conc. ppm	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	% Conv.
34	iPrCo(III)(DMG-BF <sub>2</sub> ) <sub>2</sub>	19	13400	3.68	100
35		190	1400	3.03	83
36	MeCo(III)(EMG-BF <sub>2</sub> ) <sub>2</sub>	19	4300	1.87	100
37		45 <sup>b</sup>	2100	1.69	94
38	MeCo(III)(DEG-BF <sub>2</sub> ) <sub>2</sub>	19	2900	1.58	69
39		57	920	1.65	51
40		49 <sup>b</sup>	730	1.70	82
41		48 <sup>b</sup>	900	1.78	90
42	MeCo(III)(DMG-BF <sub>2</sub> ) <sub>2</sub>	46 <sup>b</sup>	13700	2.65	100
43			14700	2.55	100

**a** 1% (w/v) SDS surfactant.

**b 30% of total complex added in MMA feed.**

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### Table 7. Emulsion Polymerisation of Other Monomers<sup>a</sup>

Example	Monomer	Complex	conc. ppm	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	% Conv
44	n-BMA	iPrCo(III)(DMG-BF <sub>2</sub> ) <sub>2</sub>	48	9800	1.8	98
45	n-BMA	MeCo(III)(DEG-BF <sub>2</sub> ) <sub>2</sub>	48	5200	2.5	97
46	n-BMA	MeCo(III)(EMG-BF <sub>2</sub> ) <sub>2</sub>	48	9400	2.5	100
47	t-BMA	MeCo(III)(DEG-BF <sub>2</sub> ) <sub>2</sub>	43	3700	2.0	100
48	PhMA	MeCo(III)(DEG-BF <sub>2</sub> ) <sub>2</sub>	43	18000	2.3	100
49	GMA	iPrCo(III)(DMG-BF <sub>2</sub> ) <sub>2</sub>	109	3500	1.8	90

<sup>a</sup> 30% of complex added with monomer feed, 1% (w/v) SDS surfactant.

**EXAMPLES 50-51****Preparation of Styrene****Initial Charge:**

	distilled water	75.03	g
5	Initiator (azobiscyanopentanoic acid)	0.1440	g
	Surfactant (10% aq. soln of sodium dodecyl sulfate)	3.14	g
	Styrene	3.59	g
	MeCo(III)(DEG-BF <sub>2</sub> ) <sub>2</sub>	0.0031	g
	Acetone	0.5	mL

10 (Complex was dissolved in acetone)

**Feed 1 (180 min @ 0.200 mL/min)**

	Styrene	33.01	g
	MeCo(III)(DEG-BF <sub>2</sub> ) <sub>2</sub>	0.0121	g
15	Acetone	1.0	mL

(Complex was dissolved in acetone)

**Feed 2 (90 min @ 0.089 mL/min)**

	Initiator (azobiscyanopentanoic acid)	0.0690	g
20	Surfactant (10% aq. soln of SDS)	8.12	g

(This solution was prepared by gently warming to 60°C)

25 Water was charged to a 5 neck, 250 mL reactor fitted with stirrer (400 rpm), condenser and thermocouple under a blanket of nitrogen. Initiator and surfactant were added to the reactor as single shots and heated to 80°C. When the reactor reached 80°C, the cobalt and styrene were added as single shots and Feed 1 commenced over 180 min. Some of the cobalt precipitated out of the monomer feed. Feed 2 (containing initiator/surfactant) was started 30 min after the start of polymerisation. The reactor was maintained at 80°C for 90 min after the completion of the monomer feed, then cooled. The reactor was sampled at 30

min intervals to monitor molecular weight and conversion .

Yield: 105.3 g stable white latex + small amount (< 0.2 g) yellow coagulum

**Table 8. Emulsion Polymerization of Styrene**

Example	Monomer	Complex	conc. ppm	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	% Conv
	Styrene	none (control)	-	130500	2.7	93
50	Styrene	MeCo(III)(DEG-BF <sub>2</sub> ) <sub>2</sub>	127	44000	3.2	94
51	Styrene	MeCo(III)(DMG-BF <sub>2</sub> ) <sub>2</sub>	127	48000	4.8	97

5

### EXAMPLE 52

#### Preparation of 60:40 MAA/MMA Macromonomer

10	Initial Charge:	Deionised Water	150 g
	Solution 1	Antrox CA897	0.6 g
		Antrox CO436	0.3 g
		Initiator WAKO V-44	0.4 g
15		iPrCo(III)(DMG-BF <sub>2</sub> ) <sub>2</sub>	8 mg
		MMA	4 g
	Solution 2:	iPrCo(III)(DMG-BF <sub>2</sub> ) <sub>2</sub>	16 mg
		MMA	44.8 g
20	Solution 3:	MAA	28.0 g

Water (150 mL) was degassed for 20 minutes with a nitrogen purge and heated to 58°C. Solution 1 was added in one shot. The feeds (solutions 2 and 3) were then added over 60 minutes. That rate of feed two was such that 5g was added over the first 20 min, 10g over the second 20 min, and the remainder over the third 20 min. The reaction was held at 58°C for 30 minutes then heated to 65°C for 1 hour and cooled. Conversion >95%, GPC molecular weight  $\bar{M}_n$  920,  $\bar{M}_w/\bar{M}_n$  1.6.

30

**EXAMPLES 53-58**

## Preparation of BMA/HEMA/MAA/MMA copolymer

5	Initial Charge	Water	75 g
		SDS (10% solution)	3 g
		4,4'-azobis(cyanovaleric acid)	141 mg
10	Solution 1:	MeCo(III)(EMG-BF <sub>2</sub> ) <sub>2</sub>	3.00 mg
		MMA	0.098 g
		MAA	0.62 g
		BMA	2.13 g
		HEMA	1.48 g
15	Solution 2:	MMA	0.562 g
		BMA	12.02 g
		MeCo(III)(EMG-BF <sub>2</sub> ) <sub>2</sub>	2.00 mg
20	Solution 3:	MAA	7.76 g
		HEMA	8.45 g

The initial charge was degassed for 30 minutes with a nitrogen purge and heated to 80°C with a preheated water bath. Solution 1 was added in one shot. Solutions 2 and 3 were then added simultaneously over 90 min. On completion of the feeds, the temperature was increased to 85°C and held for 90 min. The results of this and similar experiments are summarized in Table 9

**Table 9. Emulsion Copolymerization of MMA/MAA/BMA/HEMA**

Example	Complex	ppm	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	Conv.
53	iPrCo(III)(DMG-BF <sub>2</sub> ) <sub>2</sub>	130 <sup>a</sup>	5900	17600	2.97	100 %
54	iPrCo(III)(DMG-BF <sub>2</sub> ) <sub>2</sub>	80 <sup>b</sup>	2900	3700	1.29	100 %
55	MeCo(III)(EMG-BF <sub>2</sub> ) <sub>2</sub>	110 <sup>b</sup>	4000	11400	2.85	96 %
56	MeCo(III)(EMG-BF <sub>2</sub> ) <sub>2</sub>	50 <sup>a</sup>	4900	12600	2.53	100 %
57	MeCo(III)(DEG-BF <sub>2</sub> ) <sub>2</sub>	111 <sup>b</sup>	830	1500	1.74	96 %
58	MeCo(III)(DEG-BF <sub>2</sub> ) <sub>2</sub>	80 <sup>a</sup>	2300	3200	1.44	100 %

<sup>a</sup> All complex in solution 1.

<sup>b</sup> 40% of total complex added with Feed 1.



**EXAMPLES 59-62****Preparation of GMA-MMA macromonomer****Initial charge:**

	distilled water	75 g
5	SLS (3% solution)	5 g

**Solution 1:**

	4,4'-azobis(cyanovaleric acid)	140 mg
	GMA	2.6 g
10	MMA	1.0 g
	MeCo(III)(DEG-BF <sub>2</sub> ) <sub>2</sub>	8.9 mg

**Feed:**

	GMA	18 g
15	MMA	13.5 g
	MeCo(III)(DEG-BF <sub>2</sub> ) <sub>2</sub>	7.9 mg

20 The water-SLS mixture was vacuum degassed for 30 minutes and placed 5-neck, reactor fitted with a stirrer, condenser and a thermocouple under a blanket of nitrogen and heated to 80°C. Solution 1 was then added and the Feed commenced immediately and added over 90 minutes. The reactor was maintained at 80°C for a further 90 minutes. Conversion based on % solids was >90%.

**Table 10. Emulsion Copolymerization of MMA and GMA**

Example	Complex	ppm	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
59	iPrCo(III)(DMG-BF <sub>2</sub> ) <sub>2</sub> <sup>a</sup>	213	790	2.04
60	iPrCo(III)(DMG-BF <sub>2</sub> ) <sub>2</sub> <sup>a</sup>	135	2900	1.51
61	iPrCo(III)(DMG-BF <sub>2</sub> ) <sub>2</sub>	100	3620	2.13
62	MeCo(III)(DEG-BF <sub>2</sub> ) <sub>2</sub>	146	1460	1.55

25 a Latex unstable

**EXAMPLE 63**

## Aqueous Solution polymerization of MAA

## Initial Charge:

5	distilled water	150 g
	Initiator (WAKO VA-044)	0.3 g
	water	2 mL
	iPrCo(III)(DMG-BF <sub>2</sub> ) <sub>2</sub>	13 mg
	acetone	2 mL

10

## Feed:

	methacrylic acid	74 g
	iPrCo(III)(DMG-BF <sub>2</sub> ) <sub>2</sub>	7.5 mg

15

Water (150 mL) was charged to a 5 neck, 500 mL reactor fitted with stirrer (300 rpm), condenser and thermocouple under a blanket of nitrogen and heated to 55°C. Initiator (0.3 g dissolved in 2 mL water) and iPrCo(III)(DMG-BF<sub>2</sub>)<sub>2</sub> (13 mg dissolved in 2 mL acetone) were added to the reactor as single shots. The feed of MAA containing the remaining iPrCo(III)(DMG-BF<sub>2</sub>)<sub>2</sub> was commenced immediately (1.23 mL/min over 60 min). The reactor was maintained at 55°C for 30 min after the completion of the feed, then cooled. The methacrylic acid macromonomer was isolated by evaporation of the water.

Conversion: approx. 90%, NMR analysis indicates number average molecular weight of about 1000.

25

**EXAMPLES 64-72**

## Aqueous Solution polymerization of HEMA

30

The color of the product is dramatically lighter than similar macromonomers prepared in organic solvents (e.g., isopropanol). Complex activity is also higher.

## 35 Initial Charge:

	distilled water	52 g
	methanol	23 g

## Solution 1:

4,4'-azobis(cyanovaleric acid)	140 g
iPrCo(III)(DMG-BF <sub>2</sub> ) <sub>2</sub>	10 mg in 3.5 g HEMA

## 5 Solution 2:

HEMA	31.7 g
iPrCo(III)(DMG-BF <sub>2</sub> ) <sub>2</sub>	7 mg

10 The water-methanol mixture was charged to a 5 neck, 500 mL reactor fitted with stirrer (300 rpm), condenser and thermocouple under a blanket of nitrogen and heated to 80°C. The initiator (0.14 g dissolved in 3.5 mL HEMA) and iPrCo(III)(DMG-BF<sub>2</sub>)<sub>2</sub> were added to the reactor as a single shot. The feed of HEMA containing the remaining iPrCo(III)(DMG-BF<sub>2</sub>)<sub>2</sub> was commenced immediately and added over 90 min. The reactor was maintained at 80°C for 150 min after the completion of the feed. Further aliquots of the initiator (70 mg) were added at 1 hourly intervals. The results of these experiments are summarized in Table 11.

Table 11. Aqueous Solution Polymerization of HEMA

Example	Complex	% solids	ppm	solvent	$\bar{M}_n^a$	% Conv	Colour
64	MeCo(III)(DEG-BF <sub>2</sub> ) <sub>2</sub>	30	56 <sup>a</sup>	water	3180	93	cloudy yellow
65	iPrCo(III)(DMG-BF <sub>2</sub> ) <sub>2</sub>	30	56 <sup>a</sup>	water	1470	87	pale yellow
66	iPrCo(III)(DMG-BF <sub>2</sub> ) <sub>2</sub>	30	171 <sup>a</sup>	water	990	68	pale yellow
67	iPrCo(III)(DMG-BF <sub>2</sub> ) <sub>2</sub>	40	343	water	530	72	pale orange
68	iPrCo(III)(DMG-BF <sub>2</sub> ) <sub>2</sub>	50	400	water	490	72	pale orange
69	iPrCo(III)(DMG-BF <sub>2</sub> ) <sub>2</sub>	30	162	isopropanol	420	37	dark brown
70	iPrCo(III)(DMG-BF <sub>2</sub> ) <sub>2</sub>	30	160	70:30 water - isopropanol	590	30	brown
71	iPrCo(III)(DMG-BF <sub>2</sub> ) <sub>2</sub>	30	105	70:30 water - methanol	1610	98	pale yellow
72	iPrCo(III)(DMG-BF <sub>2</sub> ) <sub>2</sub>	30	162	70:30 water - methanol	810	68	pale yellow

20 <sup>a</sup> number average molecular weight estimated by NMR determination of the unsaturate end groups

# GENERAL PROCEDURE FOR PREPARATION OF COBALT(III) CATALYSTS

Preparation of [bis[m-[(2,3-hexanedione dioximato)(2-)-O:O']] tetrafluorodiborato  
5 (2-) -N,N',N'',N''' (methyl) (aqua) cobalt

Cobalt(III) complexes of the invention and all such complexes useful in the  
disclosed process are made by appropriate compound substitutions in the  
procedure described in Paragraph A hereafter. The same is true for Cobalt(II)  
10 complexes of the invention and of utility generally in the disclosed process. One  
skilled in the art will have no difficulty, given the disclosure that has been provided,  
in making all such complexes and in pairing the appropriate Lewis base(s) and  
cobalt-containing moieties to obtain the claimed cobalt complexes and to obtain  
the fruits of the claimed process.

15

## A. Preparation of Methyl pyridinato-Co(III)-DEG

	Methanol	50	mL
	3,4-hexanedione dioxime	3.0	g
20	CoCl <sub>2</sub> ·6H <sub>2</sub> O	2.0171	g
	Solution 1:		
	Sodium hydroxide	0.819	g
	Water	0.819	g
25	Pyridine	0.670	mL
	Solution 2:		
	Sodium hydroxide	0.532	g
	Water	0.532	g
30	Sodium borohydride	0.365	g
	Methyl bromide	0.590	mL

The methanol was degassed under nitrogen for 20 minutes at room  
temperature and the CoCl<sub>2</sub>·6H<sub>2</sub>O and the 3,4-hexanedione dioxime were added.  
35 After ten minutes the Solution 1 was added, followed by slow addition of pyridine.  
The reaction mixture was cooled to -20°C and stirring under nitrogen was  
continued for 20 minutes. The second sodium hydroxide solution and the sodium  
borohydride were added slowly. Methyl bromide was added dropwise over 20

minutes and the reaction mixture was allowed to reach room temperature. Half of the solvent was removed by evaporation and 40 mL of cold water was added. The compound was filtered and washed with a pyridine-water (5%) solution, and dried over P<sub>2</sub>O<sub>5</sub>.

5

**B: Preparation of Methyl pyridinato-Co(III)-DEG BF<sub>2</sub> Bridged.**

	Methyl pyridinato-Co(III)-DEG	3.551	g
	BF <sub>3</sub> Et <sub>2</sub> O	9.217	g
10	Ether	5	mL

The boron triethyletherate and ether were cooled under nitrogen at -20°C for 40 minutes. The methyl pyridinato-Co(III)-DEG was added over 20 minutes. The reaction was allowed to reach room temperature, then the compound was isolated by filtration and washed with ether.

15

**C: Preparation of Methyl aqua-Co(III)-DEG BF<sub>2</sub> Bridged.**

	Methyl pyridinato-Co(III)-DEG BF <sub>2</sub> bridged	3.178	g
20	Water	30	mL

The water was degassed under nitrogen at 30°C for 10 minutes. The methyl pyridinato-Co(III)-DEG BF<sub>2</sub> Bridged complex was added and the solution held at 30°C for 40 minutes. The solution was allowed to reach room temperature and the compound was isolated by filtration, and washed with water

25

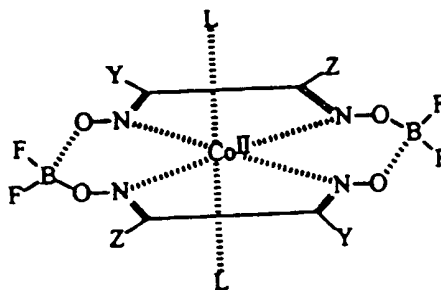
**PROCEDURE FOR PREPARING COBALT(II) CATALYSTS**

The Co(II) cobaloximes are prepared as are the Co(III) materials described above without the reaction of the intermediate with alkyl bromide, by reacting the appropriate dioxime with cobaltous chloride and bridging the reaction product with BF<sub>3</sub> etherate.

30

**CLAIMS**

1. A method for the solution or emulsion polymerization in aqueous media of at least one monomer selected from the group
- a) 1,1-disubstituted ethylenically unsaturated monomer;
  - b) styrene;
  - c) a mixture of a and b; and
  - d) a mixture of at least one of a and b with one or more other free radical polymerizable monomers;
- said monomer or monomer mixture comprising at least 50 percent by weight of monomer selected from at least one of a and b;
- comprising contacting the following materials:
- i) water or a single phase water-organic solvent mixture,
  - ii) at least one monomer selected from a to d,
  - iii) a cobalt chelate chain transfer agent,
  - iv) an optional surfactant for emulsion polymerization,
  - v) an optional free radical initiator soluble in the media;
- wherein the cobalt chelate chain transfer agent has the following properties:
- vi) hydrolytic stability, and
  - vii) solubility in water and in the organic phase, with preferential solubility in the organic phase.
2. A method according to Claim 1 wherein the cobalt chelate chain transfer agent is selected from at least one square planar cobalt(II) or cobalt(III) chelate.
3. A method according to Claim 2 wherein the cobalt chelate chain transfer agent is selected from at least one member of the group



30

$\text{Co(II)(DPG-BF}_2)_2$   
 $\text{Co(II)(DMG-BF}_2)_2$

$\text{Y}=\text{Z}=\text{Ph}$ ,  $\text{L}=\text{ligand}$   
 $\text{Y}=\text{Z}=\text{Me}$ ,  $\text{L}=\text{ligand}$



Y=Me, Z=Et, L=ligand



Y=Z=Et, L=ligand and



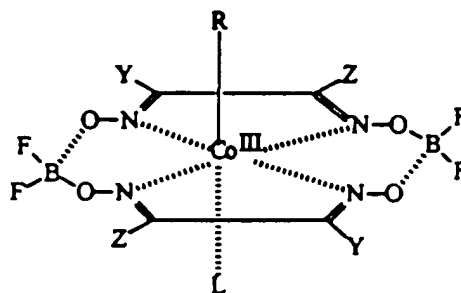
Y+Z=-(CH<sub>2</sub>)<sub>4</sub>-, L=ligand.

5 4. A method according to Claim 3 wherein the cobalt chelate chain transfer agent is Co(II) (dimethyl glyoxime-BF<sub>2</sub>)<sub>2</sub>.

5. A method according to Claim 3 wherein the cobalt chelate chain transfer agent is Co(II) (diethyl glyoxime-BF<sub>2</sub>)<sub>2</sub>.

10

6. A method according to Claim 2 wherein the cobalt chelate chain transfer agent is selected from at least one member of the group



15



Y=Z=Ph, R= alkyl, L=ligand



Y=Z=Me, R= alkyl, L=ligand



Y=Me, Z=Et, R= alkyl, L=ligand



Y=Z=Et, R= alkyl, L=ligand

20



Y+Z=-(CH<sub>2</sub>)<sub>4</sub>-, R= alkyl, L=ligand and



Y=Z=Me, R= halogen, L=ligand

7. A method according to Claim 6 wherein the cobalt chelate chain transfer agent is alkylCo(III) (dimethyl glyoxime-BF<sub>2</sub>)<sub>2</sub>.

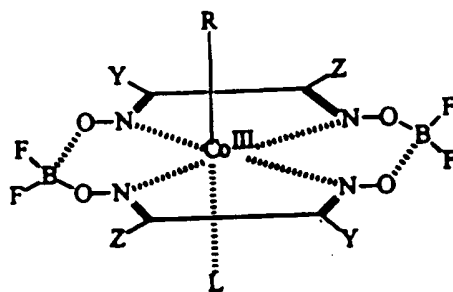
25

8. A method according to Claim 6 wherein the cobalt chelate chain transfer agent is alkylCo(III) (diethyl glyoxime-BF<sub>2</sub>)<sub>2</sub>.

9. A method according to Claim 1 wherein the polymer formed is a macromonomer.

30

10. A cobalt chelate chain transfer agent selected from the group:



comprising:

5

$\text{RCo(III)(EMG-BF}_2)_2$      $\text{Y=Me, Z=Et, R= alkyl, L=ligand;}$   
 $\text{RCo(III)(DEG-BF}_2)_2$      $\text{Y=Z=Et, R= alkyl, L=ligand; and}$   
 $\text{RCo(III)(CHG-BF}_2)_2$      $\text{Y+Z=-(CH}_2)_4-, \text{ R= alkyl, L=ligand.}$

10



## INTERNATIONAL SEARCH REPORT

Internat. Application No.

PCT/US 95/14429

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C08F2/38 C08F2/22

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 261 942 (DU PONT DE NEMOURS AND COMPANY) 30 March 1988 see the whole document ---	1-10
X	EP,A,0 199 436 (DU PONT DE NEMOURS AND COMPANY) 29 October 1986 cited in the application see claims 1-10 ---	1-10
X	US,A,4 526 945 (G. M. CARLSON) 2 July 1985 see the whole document ---	1,2,9
X	US,A,4 680 354 (JU-CHUI LIN) 14 July 1987 see the whole document ---	1,2,9
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

19 March 1996

Date of mailing of the international search report

- 4. 04. 96

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Permentier, W

# INTERNATIONAL SEARCH REPORT

Intern: al Application No  
PCT/US 95/14429

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		Relevant to claim No.
Category	Citation of document, with indication, where appropriate, of the relevant passages	
A	JOURNAL OF POLYMER SCIENCE: POLYMER CHEMISTRY EDITION, vol. 22, 1984 pages 3255-3262, A. F. BURCZYK 'COBALTOXIME AS A CATALYTIC CHAIN TRANSFER AGENT' ---	1
P,X	WO,A,95 17435 (ZENECA LTD.) 29 June 1995 see the whole document -----	1-10

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Information on patent family members

Intern: Application No

PCT/US 95/14429

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